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(54) **Method of making paper.**

(57) Disclosed is a method of making paper and paper board using a starch urea phosphate, which has a gelatinization temperature of 35 - 55 °C and contains phosphorus atoms chemically bonded to the starch in an amount of at least 0.4 % by weight and phosphorus atoms present as cold-water soluble phosphorous compounds in the starch in an amount of 0.1 % by weight or less.

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METHOD OF MAKING PAPER

FIELD OF THE INVENTION

The present invention relates to a method of making paper and paper board using a modified spray starch in order to improve paper surface strength, web strength and/or plybond strength and the like.

BRIEF EXPLANATION OF THE DRAWINGS

Fig. 1 is a Brabender Visco-Amylogram which shows the relation between temperature and viscosity to explain the gelatinization temperature of the starch.

BACKGROUND OF THE INVENTION

In making of paper and paper board, it is the usual practice to spray a slurry of starch granules to the wet web in order to improve the surface strength, web strength, and plybond strength of the paper and paper board. The starch granules entrapped by the wet web are subsequently gelatinized by heat from the machine.

Spray starch, which has been generally used in paper industry, is roughly classified into two kinds. One is raw starch (for example, corn starch, potato starch, tapioca starch and the like) and the other is modified starch (for example, starch urea phosphate, acetylated starch, and the like.).

The raw starch has a higher gelatinization temperature than the modified starch and thus cannot be sufficiently gelatinized in paper machines currently used. For example, the raw starch cannot sufficiently increase the plybond strength and thus causes ply separation of multiply paper board. In addition, since granule size of the starch is generally small except for potato starch, the raw starch granules tend to pass through the web with the process water and hence decrease the retention of the starch granules sprayed in the wet web. As a result, problems have occurred in that sufficient strength can not be given to the paper board, the paper machine being stained, and the load of the waste-water treatment system being increased.

The modified starch, particularly starch urea phosphate, usually has a gelatinization temperature which has been lowered from its original gelatinization temperature within the range of from 5 to 20 °C and thus can be sufficiently gelatinized in a drying part of prevailing paper machines. Besides, the starch urea phosphate contributes to the improvement of strength properties of paper and paper board, since starch urea phosphate sprayed in the wet web is excellently retained. It has been known, however, that the conventional starch urea phosphate has serious drawbacks. That is to say, the conventional starch urea phosphate frequently causes wire filling on a paper machine and thus leads to serious troubles, such as machine shut-down. In particular, when the pH of the pulp slurry is low, this phenomenon notably appears. The starch urea phosphate has been limited in use on account of this disadvantage. That is to say, it cannot be used in a paper machine operated in a low pH range, However, when it is necessary to maintain sufficient strength properties of paper and paper board, starch urea phosphate is of no use and in this case the paper machine must be frequently stopped to clean and change the wire. Such machine shut-down makes the paper making process costly. Commercially available starch urea phosphate which is commonly used contains phosphorus atoms chemically bonded to the starch in a quantity of 0.3 to 1.5 % by weight and phosphorus atoms present as cold-water soluble phosphorous compounds in the starch in a quantity of 0.15 to 1.5 % by weight. Modified starches other than starch urea phosphate, for example acetylated starch, having a gelatinization temperature of 35 to 55 °C are sufficiently gelatinized in a dryer part of paper machine, but the starch retention in the wet web is extremely poor and the strength properties of paper and paper board are inferior to that obtained using starch urea phosphate.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a method of making paper and paper board using a slurry of ungelatinized starch granules for spraying which have a low gelatinization temperature, exhibit an improved retention in the wet web and give sufficient strength properties of paper (for example surface strength, web strength, plybond strength, and the like) without wire filling of the paper machine in a wide pH range of the pulp slurry.

It has been ascertained from an elemental analysis of substances stuck to the wires that the wire filling in the paper machine is brought about from the deposition of insoluble aluminum phosphate by the reaction of cold-water soluble phosphorus-containing compounds in the starch with aluminum sulfate contained in the pulp slurry. In other words, it is important to reduce the content of cold-water soluble phosphorous compounds in the starch as far as possible. Furthermore, it has been discov-

ered that the strength properties of paper and paper board and the retention of the sprayed starch are improved as the content of phosphorus atoms bonded to the starch is increased.

It has, also, been found that the paper strength is strongly related to the gelatinization temperature of the starch used.

Thus, the present invention provides a starch urea phosphate for paper making which has a gelatinization temperature of 35 to 55 °C and contains phosphorus atoms chemically bonded to the starch in an amount of at least 0.4 % by weight, and phosphorus atoms present as cold-water soluble phosphorous compounds in the starch in an amount of 0.1% by weight or less.

DETAILED DESCRIPTION OF THE INVENTION

It is essential that the content of phosphorus atoms chemically bonded with starch is 0.4 % by weight or more. The maximum content of phosphorus atoms bonded with starch is not specially limited, but an increase of a quantity of phosphoric acid, salts thereof and the like added in a reaction mixture tends to increase the quantity of non-reacted phosphorous compounds in the starch, so that it is natural that the content of phosphorus atoms does not exceed 5 % by weight. On the other hand, if the content is less than 0.4 % by weight, sufficient retention of starch granules sprayed in the wet web cannot be achieved and excellent strength properties of paper cannot be given to the paper. The content of phosphorus atoms chemically bonded to the starch is preferably 0.4 to 3 % by weight.

In addition, it is essential that the starch urea phosphate contains phosphorus atoms present as cold-water soluble phosphorous compounds in the starch (e.g. sodium-, potassium- or ammonium salt and the like of phosphoric acid, phosphorous acid and the like) in a content of 0.1 % by weight or less. If the content is more than 0.1 % by weight, insoluble substances are formed in the pulp slurry to cause wire filling on the paper machine. The term "cold-water" herein is water having a temperature of less than room temperature.

In addition, the gelatinization temperature of the starch urea phosphate according to the present invention is 35 to 55 °C, preferably 40 to 50 °C. If the gelatinization temperature is lower than 35 °C, the starch granules stored in a storage tank may be unnecessarily gelatinized because the temperature often rises to a value above 35 °C during storage. If the gelatinization temperature is higher than 55 °C, the starch granules do not gelatinize sufficiently during the prevailing drying process of the paper machine.

The method of producing the starch urea phosphate according to the present invention is basically conventional.

The method, however, must be slightly modified in order to satisfy the claimed ranges. If a dry method wherein starch is mixed with a combination of phosphoric acid or a phosphate and urea and then heated is selected, its reaction conditions are made more severe than those of the prevailing process. Thus, the reaction is conducted at a temperature of 80 - 150 °C for 30 minutes to 5 hours, using 2 to 20 parts by weight of urea and 1 to 15 parts by weight of phosphoric acid or a phosphate based on 100 parts by weight of the starch.

The starch used as raw material in the present invention includes corn starch, tapioca starch, potato starch, sweet-potato starch, wheat starch and the like. In addition, it may be partially and/or perfectly (completely) subjected to a treatment of esterification, etherification, oxidation and the like.

In the method of the present invention, phosphoric acid or a phosphate to be used is not specially limited, but phosphoric acid, phosphorous acid and primary, secondary and/or tertiary sodium-, potassium- and/or ammonium salts thereof can be used.

In addition, acids other than the above described phosphoric acid, salts thereof and the like can be used together with the phosphoric acid and phosphates. For example, hydrochloric acid, sulfuric acid, nitric acid, sulfamic acid, maleic acid, succinic acid and acetic acid and salts thereof can be used. Also oxidizing agents can be used. For example, hydrogen peroxide, ammonium persulfate and the like can be used.

When the starch urea phosphate according to the present invention is sprayed onto the wet web, it can be used together with raw starch, polyacrylamide, polyvinyl alcohol, polyethyleneimine, polyethyleneoxide and the like.

As to the method of spraying in the present invention, in preferred practice on the wire part of the paper machine, the starch slurry having a concentration of about 0.1 to 5 % is sprayed onto the paper and paper board web by means of spray nozzles fixed in a spray pipe mounted across the wire. Subsequently, the sprayed wet web is dewatered by suction and pressed to dewater, followed by drying in a dryer to obtain the paper, paper board and the like. In the laboratory in the same manner as in the usual case, pulp slurry of which freeness is adjusted by a laboratory beater is placed in an experimental paper machine and dewatered to make web. A starch slurry is sprayed onto the web. A second wet web is placed on the sprayed side of said wet web. The combined web is dewatered by suction to 80 % water content, pressed for further dewatering, and dried on a

drum dryer at a desired temperature to obtain the paper and paper board.

In the present specification, the gelatinization temperature is the temperature at which a tangetial line of the temperature/viscosity curve of the Brabender Amylogram left from the base line first makes an angle of 45 ° against the base line, as shown in Fig.1. In this case, the starch-concentration is set at 25 % by weight.

The present invention provides a starch suitable for paper making. The starch does not deposit insoluble substances on the wire even in a pulp slurry having a low pH, thus effectively preventing wire filling on a paper machine.

EXAMPLE

The present invention will be illustrated in more detail with reference to the preferred examples. However, the present invention is not limited by these preferred examples.

Production Example 1

10 parts urea were dissolved in 10 parts water and the resulting solution was stirred together with 2.7 parts of 75 % phosphoric acid followed by spraying the resulting solution in 100 parts corn starch with mixing. The resulting mixture was heated and reacted at 140 °C for 3 hours in a hot air drier. The gelatinization temperature of the reaction product was 41 °C which was measured by the Amylograph at a starch-concentration of 25% by weight.

The quantity of phosphorus atoms which are bonded to the starch was 0.86 % by weight based on the dry product and the quantity of phosphorus atoms present as cold-water soluble phosphorous compounds in the starch was 0.08 % by weight, as the result of an elemental analysis. Hereinafter this product is referred to as product A.

Production Example 2

10 parts urea were dissolved in 10 parts water and the resulting solution was stirred together with 2.2. parts 75 % phosphoric acid followed by spraying the resulting solution overloo parts tapioca starch with mixing. The resulting mixture was heated and reacted at 140 °C for 2.5 hours in a hot air drier. The gelatinization temperature of the reaction product was 45 °C.

The quantity of phosphorus atoms which are bonded to the starch was 0.51 % by weight (based on the dry product) and the quantity of phosphorous atoms present as cold-water soluble phosphorous compounds in the starch was 0.06 % by weight (based on the dry product) as the result of an elemental analysis. Hereinafter this product is referred to as product B.

Production Example 3

10 parts urea were dissolved in 10 parts water and the resulting solution was stirred together with 1.9 parts 75 % phosphoric acid followed by spraying the resulting solution over 100 parts hydroxyethylated corn starch with mixing. The resulting mixture was heated and reacted at 140 °C for 3 hours in a hot air drier. The gelatinization temperature of the reaction product was 42° C. The quantity of phosphorus atoms which are bonded to the starch was 0.43 % by weight (based on the dry product) and the quantity of phosphorus atoms present as cold-water soluble phosphorous compounds in the starch was 0.06 % by weight (based on the dry product) as the result of an elemental analysis. Hereinafter this product is referred to as product C.

Production Example 4

8 parts urea were dissolved in 8 parts water and the resulting solution was stirred together with 1.7 parts 75 % phosphoric acid followed by spraying the resulting solution over 100 parts corn starch with mixing. The resulting mixture was heated and reacted at 140° C for 2.5 hours in a hot air drier. The gelatinization temperature of the reaction product was 53° C.

The quantity of phosphorus atoms which are chemically bonded to the starch was 0.42 % by weight (based on the dry product) and the quantity of phosphorus atoms present as cold-water soluble phosphorous compounds in the starch was 0.08 % by weight (based on the dry product) as the result of an elemental analysis. Hereinafter this product is referred to as product D.

Example 1

Aluminium sulfate was added to 375 ml of a 1 % pulp slurry of a needle-leaved tree breached kraft pulp (NBKP) having a freeness (CSF) of 340 ml in a quantity of 1.0 % based on the pulp and the resulting mixture was diluted until 0.03 % in an experimental square type paper machine (25 cm x 25 cm). Then, the diluted mixture was dewatered to produce a web and stopped at a point of time when the level of water of the pulp slurry reached 2

cm over the wire, followed by spraying a 1 % slurry of starch shown in Table 1 over the pulp slurry surface, so that the starch will be applied in a quantity of 2 g/m^2 based on the dry product. Then, the dewatering was started again to obtain a wet web (having a basis weight of 60 g/m^2) as a first ply. Next, a wet web (NBKP/LBKP/waste corrugated paper board = 50/20/30; CSF = 390 ml; no starch applied) as a second ply obtained in the same manner as said wet web as the first ply was put upon the surface of the first ply, to which the starch had been applied, and then subjected to dewatering by suction and by pressing, followed by heating at 75 °C for 60 seconds in the cylinder drier, whereby a sample was obtained.

The plybond strength and the retention of starch of this sample were measured by the following methods:

1) Plybond strength (90° separation method)

One side of the test piece (10 cm x 1 cm) was adhered to a metallic plate from which the aimed layer was previously separated by 2 to 3 cm and then pulled in the direction of 90 ° by means of the tensile tester to carry out the separation, whereby measuring the resisting force.

2) Retention of starch

Provided that a quantity of starch contained in the product determined by the Anthrone's sulfuric acid method is A and a quantity of starch sprayed is B, the retention of starch was calculated by the following equation:

Retention (%) = [A(g/m^2)/B(g/m^2)] x 100

Table 1

Name of starch	Content of phosphorus atoms bonded with starch (%)	Content of phosphorus atoms present as cold-water soluble phosphorous compounds in the starch (%)	Gelatinization temperature (°C)	Plybond strength 1) (g/cm)	Retention of starch 2) (%)
Product A	0.66	0.08	41	152	95
Product B	0.51	0.06	45	146	94
Product C	0.43	0.06	42	142	85
Product D	0.42	0.08	53	138	84
Corn starch urea phosphate A	0.72	0.59	40	149	96
Corn starch urea phosphate B	0.51	0.31	43	150	95
Corn starch urea phosphate C	0.44	0.14	41	140	86
Corn starch urea phosphate D	0.36	0.05	42	118	72
Corn starch urea phosphate E	0.10	0.08	60	79	70
Raw corn starch	-	-	66	77	71
Raw tapioca starch	-	-	65	74	69
Raw potato starch	0.06	-	60	84	91

Table 1 continued

Name of starch	Content of phosphorus atoms bonded with starch (%)	Content of phosphorus atoms present as cold-water soluble phosphorous compounds in the starch (%)	Gelatinization temperature (°C)	Plybond strength 1) (g/cm)	Retention of starch 2) (%)
Acetylated corn starch	-	-	52	102	70
Acetylated potato starch	-	-	51	106	90
Cationized corn starch	-	-	42	108	71
Hydroxyethyl corn starch	-	-	53	97	69

It was found from Table 1 that the starch having the gelatinization temperature of 60°C or more showed an unsatisfactory value in view of the plybond strength. In addition, the starch urea phosphate containing phosphorus atoms bonded with starch in a quantity of 0.36 % or less and having the gelatinization temperature of 42°C, or the starch of which a gelatinization starting temperature was reduced by the acetylation and the like, exhibited an improved strength in comparison with the starch having the gelatinization temperature of 60°C or more; it is, however, still insufficient. The starch urea phosphate including starch according to the present invention having the reduced gelatinization temperature and containing phosphorus atoms bonded with starch in a quantity of 0.42 % or more only exhibited the satisfactory plybond strength.

On the other hand, potato starch or modified starch therefrom and the starch urea phosphate including starch according to the present invention containing phosphorus atoms bonded with starch in a quantity of 0.42 % or more exhibited the superior value in view of the retention of starch.

It is found from the above that only the starch urea phosphate including starch according to the present invention having the reduced gelatinization temperature and containing phosphorus atoms bonded with starch in a quantity of 0.42 % or more exhibits satisfactory results in view of both plybond strength and retention of starch.

Example 2

Starch shown in Table 2 was sprayed between the first ply (pH 4.3) and the second ply (pH 6.5) in a quantity of 2 g/m^2 on a cylinder machine (web width: 1,660 mm; paper velocity: 96 m/min) to obtain white paper board having a basis weight of 450 g/m^2.

Example 3

Starch shown in Table 3 was sprayed on a pulp slurry having a pH of 4.4 on the wire in a quantity of 0.5 g/m^2 on a foundrinier paper machine (web width: 3,700 mm; paper velocity: 420 m/min) to obtain mechanical paper having a basis weight of 82 g/m^2.

Table 2

Name of starch	Content of phosphorus atoms bonded with starch (%)	Content of phosphorus atoms present as cold-water soluble phosphorous compounds in the starch (%)	Gelatinization temperature (°C)	Plybond strength 1) (g/cm)	Wire filling
Product A	0.66	0.08	41	141	no
Product B	0.51	0.06	45	139	no
Product C	0.43	0.05	42	130	no
Corn starch urea phosphate A	0.72	0.59	40	142	on the 3rd day
Corn starch urea phosphate B	0.51	0.31	43	137	on the 5th day
Corn starch urea phosphate C	0.44	0.14	41	129	on the 10th day
Raw corn starch	-	-	66	79	no

Table 3

Name of starch	Content of phosphorus atoms bond with starch (%)	Content of phosphorus atoms present as cold-water soluble phosphorous compounds in the starch (%)	Gelatinization temperature (°C)	Bursting strength 1) (g/cm)	Tensil strength 2) (Kgf/15mm)	Wire filling
Product B	0.51	0.06	45	2.04	7.0	no
Raw corn starch	-	-	66	1.60	5.4	no
Corn starch urea phosphate A	0.72	0.59	40	1.97	6.9	on the 3rd day
Corn starch urea phosphate C	0.44	0.14	41	1.82	6.0	on the 9th day

: (1) Bursting strength ---This was measured by means of the Mullen burst tester in accordance with JIS P8112.
(2) Tensile strength --- This was measured by means of the tensile tester in accordance with JIS P8113.

As shown in Table 2, all of the starch urea phosphate including starch according to the present invention containing phosphorus atoms bonded with starch in a quantity of 0.42 % or more exhibited the superior plybond strength in comparison with cornstarch. However, the starch urea phosphate of which a cold-water soluble phosphorous compounds contains phosphorus atoms in an amount of 0.14 % by weight or more, i.e. the urea-phosphated starch outside the claimed range, brought about the wire filling within 3 to 10 days and therefore the machine had to be stopped and cleaned. On the contrary, the starch according to the present invention did not bring about the wire filling even after the continuous operation of one month or more.

The starch according to the present invention can exhibit satisfactory properties in view of both plybond strength and the wire filling and thus it can be said to be the ideal spray starch.

Merely product B (having a gelatinization temperature of 45°C and containing phosphorus atoms bonded with starch in a quantity of 0.51 %, of which a cold-water soluble phosphorous compound had phosphorus atoms of 0.06 % by weight), exhibited superior results in various kinds of physical properties shown in Table 3 and did not bring about the wire filling.

Claims

1. A method of making paper and paper board, comprising the steps of spraying a slurry of ungelatinized starch granules to a wet web of paper fibers, dewatering said web, and heating said web to assist the gelatinization of the starch granules, wherein said starch granules are starch urea phosphate granules, which have a gelatinization temperature of 35 - 5°C and contain phosphorus atoms chemically bonded to the starch in an amount of at least 0.4% by weight and phosphorus atoms present as cold-water soluble phosphorous compounds in the starch in an amount of 0.1 % by weight or less.

2. A method according to Claim 1 wherein the amount of the phosphorus atoms chemically bonded to said starch is within the range of 0.4 to 3 % by weight.

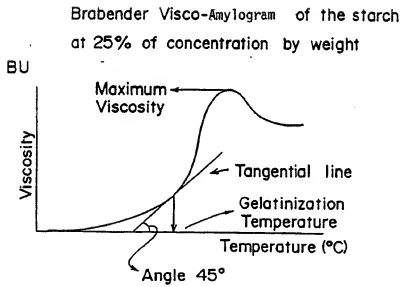
3. A method according to Claim 1 wherein said gelatinization temperature is within the range of 40 to 50°C.

4. A method according to Claim 1 wherein said granules are prepared by mixing 100 parts by weight of raw starch with 2 to 20 parts by weight of urea and 1 to 15 parts by weight of phosphoric acid or a phosphate thereof, and then reacting at 80 - 150°C for 30 minutes to 5 hours.

5. A method according to Claim 4 wherein said raw starch is selected from the group consisting of corn starch, tapioca starch, potato starch and wheat starch.

6. A method according to any of the preceding Claims in which said starch granules are sprayed to the wet web in an amount of 0.2 - 20 g/m^2.

Fig. 1



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EUROPEAN SEARCH REPORT

Application Number

EP 90 11 6567

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-3 459 632 (C G CALDWELL ET AL) * column 11, lines 1 - 47; claims 1-9 *	1-6	D 21 H 19/54 D 21 H 17/28
X	DATABASE WPIL,nØ 87-188027,Derwent Publications & JP-A-62116602(SANWA DENPUN) 28-05-87 * The entire abstract *	1-6	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

D 21 H

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	11 December 90	FOUQUIER J.P.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
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A: technological background
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E: earlier patent document, but published on, or after the filing date
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